THE ASSOCIATION OF BENZOIC ACID IN SOLUTION

BY

PRINCE EARL ROUSE, JR.

A.B., Central College, 1938

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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ACKNOWLEDGMENT

The author wishes to express his appreciation of the assistance of Dr. F. T. Wall and Professor W. H. Rodebush under whose supervision this investigation was made. He wishes to thank Professor T. E. Phipps for several helpful conversations and Dr. C. E. Holley, Jr. for his aid on several occasions.

THE ASSOCIATION OF BENZOIC ACID IN SOLUTION

Beckmann[1] found from cryoscopic and ebullioscopic measurements of molecular weight that benzoic acid in benzene and other inert solvents was largely dimerized. Since then many investigators have studied the properties of carboxylic acids to find the degree of association in solution and in the vapor phase. The methods used include determination of freezing point depressions[2,3], boiling point elevations[4], distribution coefficients[5], vapor densities[2,6], electron diffraction[7], and infra-red absorption spectra.[8] The present investigation uses an indirect method of measuring the vapor pressure lowering of a solution of benzoic acid in benzene. The method is essentially that of Barger[9] as modified by Signer[10] and Lassettre and Dickinson[11] and depends on the distribution of a volatile solvent between two non-volatile solutes.

The apparatus used consisted of a U-tube joining two bulbs, each of which had a graduated side arm sealed into it at right angles to the U-bend. A solution of benzoic acid in benzene was placed in one bulb and a solution of phenanthrene in benzene was placed in the other bulb. The apparatus was evacuated, care being taken to outgas the solutions thoroughly. The vapor pressures of the two solutions were allowed to come to equilibrium by distillation of the solvent vapor through the U-tube. The equilibrium volumes of the solutions were read by tilting the apparatus so that the solutions flowed into graduated side arms.

From the equilibrium volumes of the solutions and the weights of the two solutes the apparent molecular weight M of the benzoic acid was calculated. The dissociation constant K of the dimer was found in each case and the equation

$$\log_{10}K = 3.790 - \frac{1977}{T}$$

was found to express $\log_{10}K$ as a function of the absolute temperature T. The probable error in the value of $\log_{10}K$ calculated from the equation is about 0.6%. The heat of dissociation of the dimer of benzoic acid was found from the slope of this straight line to be 9040 $\pm$ 400 calories per mole.

The results are given in the following table in whcih C represents the concentration of the benzoic acid solution in weight per cent solute.

Experiment	Temp. °K.	C	M	$-\log_{10}K$
1.	305.3	2.763	229.2	2.741
2.	305.3	1.357	224.6	2.789
3.	305.8	4.410	231.0	2.660
4.	305.8	3.095	228.7	2.658
5.	305.8	3.923	230.0	2.642
6.	305.8	3.065	227.4	2.586
7.	305.9	1.041	218.8	2.645
1.	316.9	2.735	223.6	2.442
2.	316.6	1.340	218.6	2.534
3.	317.1	4.380	227.0	2.413
4.	317.1	3.083	225.6	2.488
5.	317.1	3.893	226.0	2.408
6.	317.1	3.054	224.3	2.431
7.	317.1	1.027	212.4	2.421
1.	329.3	2.713	218.9	2.245
2.	329.3	1.319	210.5	2.254
3.	330.0	4.336	221.0	2.130
4.	330.0	3.064	220.9	2.275
5.	330.0	3.862	220.4	2.153
6.	330.0	3.036	219.5	2.219
7.	330.0	1.009	203.4	2.155

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VITA

The author was born at Bucklin, Missouri, on October 12, 1917. He received his elementary education in the public schools of that city and was graduated from Bucklin High School in May, 1934. He attended Central College at Fayette, Missouri from 1934 to 1938, receiving the degree of Bachelor of Arts in June, 1938. The author attended the Graduate School of the University of Illinois from 1938 to 1941, holding a graduate assistantship in physical chemistry the first year, a University Fellowship the second year, and the du Pont Fellowship the third year. He is a member of Sigma Xi, Phi Lambda Upsilon, and Phi Beta Kappa.

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